(12) UK Patent Application (19) GB (11) 2 085 756 A

(21) Application No 8124364
(22) Date of filing 10 Aug 1981
(30) Priority data
(31) 55/112082
(32) 14 Aug 1980
(33) Japan (JP)
(43) Application published
6 May 1982
(51) INT CL³
G03C 1/76
B32B 27/30 29/00
(52) Domestic classification
B2E 1715 404S 473T
509T 520T M
C1A 322 510 N34 VF1
G2C C19H4
(56) Documents cited
None
(58) Field of search
B2E
C3L
(71) Applicants
Fuji Photo Film Co., Ltd.
No. 210, Nakanuma
Minami Ashigara-shi
Kanagawa
Japan
(72) Inventor
Yasuzi Asao
(74) Agents
Gee & Co.,
Chancery House,
Chancery Lane,
London WC2A 1QU.

(54) Coated paper supports for photographic printing paper

(57) A support sheet consists of a paper sheet coated with a layer, e.g. 5 to 200 μ thick, of a polyolefin, e.g. polyethylene or polypropylene, in which are dispersed titanium oxide particles coated with a dihydric, trihydric or tetrahydric alcohol.

Preferred alcohols contain 2 to 18, e.g. 2 to 6, C atoms and 2 to 4 methylol groups, e.g. trimethylolethane. Preferred ratios are 0.01 to 10 wt. % of alcohol to TiO_2, and 1 to 40 wt. % of TiO_2 to polyolefin.

The anastase or rutile TiO_2 may be pre-coated with silica or alumina and then is sprayed with or dipped into the alcohol. The coating mixture is extrusion coated at a die temperature of 250° to 350°C at a paper travelling speed of 50 to 500 m/minute.

The support is coated on its coated surface with a silver halide photographic emulsion to make a photographic printing paper which is shown by a microphotometer to have high resolving power.

GB 2 085 756 A

2085756

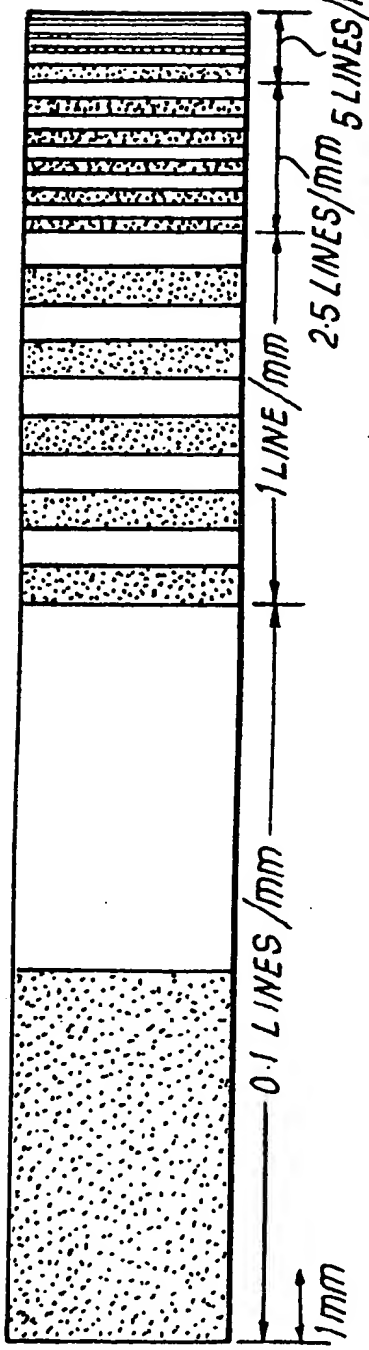

FIG. 1

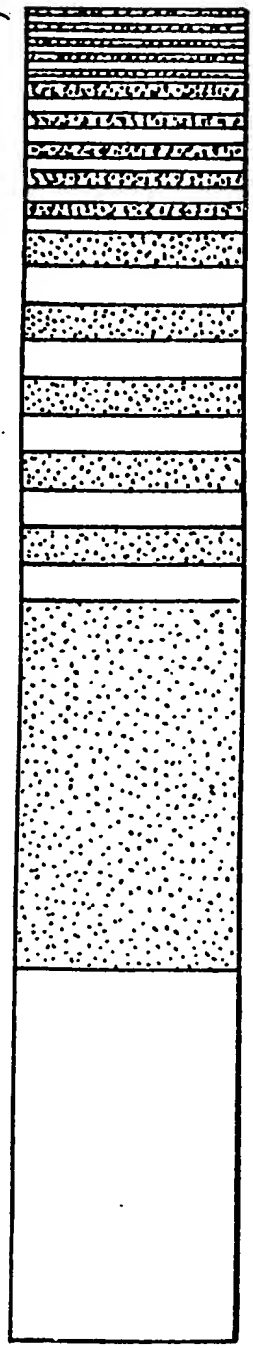

FIG. 2

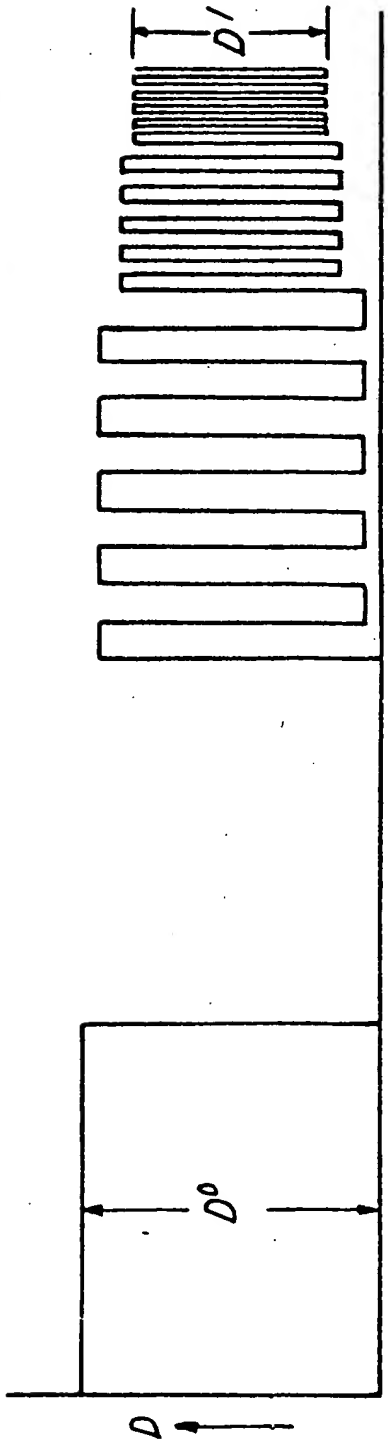

FIG. 3

SPECIFICATION

Coated paper supports for photographic printing paper

The present invention relates to coated paper sheets used as supports for light-sensitive photographic papers. More specifically, it relates to such coated paper used for photographic printing paper which has a high resolving power for print images.

As the surface coating on paper supports for photographic printing paper, there has recently been used, in place of the traditional barium sulfate layer (for "baryta paper"), a layer of a polyolefin containing dispersed titanium oxide pigment. This layer is coated on the surface to which a light-sensitive silver halide photographic emulsion is to be applied, and the layer has high whiteness and hiding power.

The titanium oxide pigment can be used in unmodified form, or the surface of the titanium oxide particles can be coated with an inorganic substance such as silica or aluminium. However, photographic printing papers incorporating supports of either of these types are unsatisfactory since they have a low resolving power of print images. Further, it has been generally well known to add a surface active agent in the form of a metal soap such as calcium stearate or zinc palmitate in order to improve the dispersibility of the titanium oxide pigment in the polyolefin. However, in photographic printing papers having such supports, the resolving power of print images although somewhat improved, is unsatisfactory.

An object of the present invention is to provide a polyolefin coated support for use in making photographic printing paper which has a high resolving power of print images.

According to the present invention, a paper sheet support for a photographic printing paper comprises a paper sheet on which is coated by extrusion a layer of a polyolefin in which are dispersed titanium oxide pigment particles which are coated with a dihydric, trihydric or tetrahydric alcohol.

Examples of di-, tri- and tetrahydric (together referred to as polyhydric) alcohols which can be used in the present invention, include those which have two hydroxyl groups in the molecule such as ethylene glycol, propylene glycol, 1,3 - dihydroxybutane, 1,4 - dihydroxybutane, pentamethylene glycol, 2,5 - dihydroxyhexane, 2,4 - dihydroxy - 2 - methylpentane, heptamethylene glycol or dodecamethylene glycol, those which have three hydroxyl groups in the molecule such as trimethylolethane, trimethylolpropane, glycerine, 2,4 - dihydroxy - 3 - hydroxymethylpentane, 1,2,6 - hexanetriol or 2,2 - bis - (hydroxymethyl) - 3 - butanol, and those which have four hydroxyl groups in the molecule such as pentaerythritol.

When only a single hydroxyl group is present in a molecule or when 5 or more hydroxyl groups are present in the molecule, the resolving power of print images of the resulting photographic printing paper is not improved.

It is believed that the resolving power of print images is improved when using the coated paper of the present invention for printing paper because the dispersibility of the titanium oxide pigment in the polyolefin is improved, which increases the hiding power of the polyolefin layer.

It has been found that the coated paper of the present invention is very suitable for producing printing paper in that it causes less fogging in addition to having the above described effect.

The preferred amount of the polyhydric alcohol in the coating is in the range of 0.01 to 10% by weight; a more preferred amount is in the range of 0.1 to 1.5% by weight. If the coating contains less than 0.01% by weight of the polyhydric alcohol, the resolving power of print images on the photographic printing paper is hardly improved. Although the resolving power can be improved with increase in the amount of the coating, an amount of more than 10% by weight is not suitable because the working environment deteriorates by an increase in the generation of smoke or an offensive smell during the extrusion operation.

The polyhydric alcohols used in the present invention preferably have 2 to 18 carbon atoms in the molecule. Polyhydric alcohols having 2 to 4 methylol groups and 2 to 6 carbon atoms in a molecule are preferably used, and those having three methylol groups and 4 to 5 carbon atoms in the molecule are more preferably used. When using a titanium oxide pigment wherein the surface of particles was coated with trimethylolethane, the photographic printing paper has the most improved resolving power of print images.

In order to apply the polyhydric alcohol to the surface of particles of the titanium oxide pigment, it is preferable to use a process which comprises dipping titanium oxide in a solution of polyhydric alcohol, evaporating the solvent and drying. Another preferred process comprises spraying a solution of polyhydric alcohol in a solvent on titanium oxide, removing the solvent and drying, and still another preferred process comprises mixing titanium oxide with polyhydric alcohol which is changed into a liquid. In these processes, it is particularly preferred to use the process which comprises mixing titanium oxide with polyhydric alcohol and powdering it. For example, the polyhydric alcohol is added to titanium oxide when it is powdered by a fluid energy crusher such as a micronizer or jet mill. Further, a process which comprises uniformly blending by means of a high shear mixer such as a Henschel mixer or a super mixer, may be used.

Any titanium oxide, having an anatase structure or a rutile structure may be used in the present invention. The titanium oxide particles can be uncoated or their surface can be coated with an inorganic substance such as silica or alumina. It is preferably to use titanium oxide having a heat loss of 0.8% by weight or less when heated at 300°C for 3 hours; if the heat loss is more than 0.8%, the resolving power

deteriorates. The titanium oxide pigment is preferably present in an amount of 1 to 40% by weight, more preferably, 5 to 20% by weight, based on the polyolefin resin.

Preferably, a masterbatch is first produced of polyolefin containing titanium oxide pigment, the surface of the particles being coated with polyhydric alcohol. The masterbatch is mixed with further polyolefin prior to extrusion in the proportion of titanium oxide pigment to the polyolefin in the masterbatch is preferably in the range of 20 to 60% by weight and, more preferably 10 to 40% by weight. The masterbatch may be produced by any process, but it is most preferable to use a fusion mixing process by means of, for example, an extruder for blending, a heat kneading roll, a Banbury mixer or a kneader.

Examples of the polyolefins usable in the present invention include low density polyethylene, high density polyethylene, polypropylene and blends thereof. Of the above polyolefins, low density polyethylene is preferred.

The thickness of the coating layer is preferably 5 to 200μ, more preferably 10 to 40μ. The layer may also contain a known fluorescent whitening agent, antioxidant, antistatic agent and/or release agent.

Examples of the paper used as the support include those composed of natural pulp, synthetic pulp or mixtures thereof. The paper has a thickness of preferably 20 to 400 microns, more preferably 70 to 250 microns. The paper has a basis weight of preferably 15 to 350 g/m^2, more preferably, a basis weight of 50 to 200 g/m^2.

The paper may also contain a number of known additives, including strengthening agents, sizing agents, coloring agents and fluorescent whitening agents.

The coating is applied by extrusion coating, namely by coating a travelling paper sheet with the polyolefin composition which is extruded as a molten film from an extruder through a die with fusing. The fusing temperature of the polyolefin in the die is 250° to 350° and preferably 280° to 320°C. The travelling speed of the paper is preferably 50 to 500 metres/minute, more preferably 80 to 250 m/minute.

A silver halide photographic emulsion (e.g. in a gelatin binder) can then be applied to the polyolefin layer, to make a photographic printing paper.

Figures 1, 2 and 3 of the drawings show respectively a minute line chart (×10) for measuring resolving power, a minute line print image (×10) and an optical density measured by a microphotometer.

The resolving power is shown as a value obtained by the formula $(D_1/D_0)\times 100$ (%).

The method of measuring the resolving power in the examples was as follows.

After a photographic emulsion was applied to a polyolefin coated paper, a minute line chart (Fig. 1) for measuring a resolving power was printed out thereon. The optical density difference of the minute line print image (Fig. 2) was measured by a microphotometer produced by Union Kogaku Co., and the resolving power was shown as a value obtained by the following formula. This value is in accordance with the value is, the higher the resolving power is.

$$\text{Resolving power (\%)} = \frac{\text{Optical density difference of a minute line print image of 5 lines/mm between the exposed part and the non-exposed part}}{\text{Optical density difference of a minute line print image of 0.1 lines/mm between the exposed part and the non-exposed part}} \times 100$$

EXAMPLE 1

The paper used was composed of 100% LBKP (Laubholz Bleach Kraft Pulp) having a basis weight of 175 g/m^2 and a thickness of 180. Polyethylene having a density of 0.920 g/cc and a melt index of 5.0 g/10 minutes was applied to the paper by extrusion coating so as to have a thickness of 30μ. The polyethylene had the following compositions (A) to (H). In the following compositions (A) to (H), the compositions (A) to (C), (G) and (H) are for comparison and the compositions (D) to (F) are examples of the present invention.

(A) A paper to which was added an anatase type titanium oxide as the only pigment.

(B) A paper to which was added an anatase type titanium oxide pigment and calcium stearate as a dispersing agent.

(C) A paper to which was added an anatase type titanium oxide pigment and zinc stearate as a dispersing agent.

(D) A paper to which was added an anatase type titanium oxide pigment which was prepared by dipping the pigment in a solution of 2,4 - dihydroxy - 2 - methylpentane in ethanol, evaporating the ethanol and drying to coat the surface of the pigment particles with 2,4 - dihydroxy - 2 - methylpentane.

(E) A paper to which was added an anatase type titanium oxide pigment coated with trimethylolpropane which was prepared by mixing trimethylol propane and an anatase type titanium oxide pigment and powdering by a jet mill.

(F) A paper to which was added an anatase type titanium oxide pigment coated with trimethylolethane which was prepared by mixing trimethylolethane and an anatase type titanium oxide pigment and powdering by a jet mill.

(G) A paper to which was added an anatase type titanium oxide pigment coated with butanol which was prepared by mixing butanol and an anatase type titanium oxide pigment and powdering by a jet mill.

(H) A paper to which was added an anatase type titanium oxide pigment coated with glucose which was prepared by mixing glucose and an anatase type titanium oxide pigment and powdering by a jet mill.

The titanium oxide pigments were added in an amount of 10% by weight based on polyethylene, respectively.

After the surface of the resulting polyethylene resin coated paper was subjected to a corona discharge treatment, a silver halide photographic emulsion was applied thereto. A minute line chart for measuring a resolving power was printed out thereon, and the resolving power was measured.

Table 1

Experiment No.		Composition of Polyethylene	Surface Active Agent or Polyhydric Alcohol	Amount Added or Amount Applied (Based on Titanium Oxide Pigment, % by Weight)	Resolving Power (%)
1	(A)		None	0	47.5
2	(B)		Calcium Stearate	0.02	48.0
3	(B)		"	0.5	50.4
4	(B)		"	1.5	50.8
5	(C)		Zinc Stearate	0.02	48.5
6	(C)		"	0.5	50.5
7	(C)		"	1.5	50.8
8	(D)	(This Invention)	2,4-Dihydroxy-2-methyl-pentane	0.02	52.0
9	(D)	"	"	0.5	53.5
10	(D)	"	"	1.5	53.6
11	(E)	"	Trimethylolpropane	0.02	52.5
12	(E)	"	"	0.5	53.8
13	(E)	"	"	1.5	53.9
14	(F)	(This Invention)	Trimethylolthane	0.02	53.5
15	(F)	"	"	0.5	55.9
16	(F)	"	"	1.5	56.0
17	(G)		Butanol	0.02	47.6
18	(G)		"	0.5	47.7
19	(G)		"	1.5	47.7
20	(H)		Glucose	0.02	48.5
21	(H)		"	0.5	49.5
22	(H)		"	1.5	49.8

EXAMPLE 2

Masterbatches of the composition (A), (C) and (F) in Example 1 were produced by means of a kneader (pressure kneader TD3 - 5 produced by Toshin Sangyo Co.). Titanium oxide pigment was added to each masterbatch in an amount of 40% by weight based on the polyethylene and amounts of zinc stearate and trimethylolethane added were 0.5% by weight, based on the titanium oxide pigment, respectively. Thereafter, the masterbatches were diluted so that the amount of the titanium oxide pigment was 10% by weight based on polyethylene. The masterbatches were then applied to a base paper composed of LBKP 100% having an areal weight of 175 g/m² and a thickness of 180 μ by extrusion coating. The thickness of the polyethylene layer was 30 μ. The polyethylene used had a density of 0.920 g/cc and a melt index of 5.0 g/10 minutes.

After the surface of the resulting polyethylene-coated paper was subjected to a corona discharge processing, a silver halide photographic emulsion was applied thereto and the resolving power was measured. Results are as shown in Table 2. The results clearly show that a high resolving power is obtained when using titanium oxide pigment coated with trimethylolethane, even if it is only mixed for a short time by the kneader.

Table 2

Composition of Polyethylene	Surface Active Agent or Polyhydric Alcohol	Resolving Power (%) Mixing Time in Kneader 15 Minutes	30 Minutes	60 Minutes
(A)	None	30.5	38.5	47.5
(C)	Zinc Stearate	35.0	42.3	50.5
(F)	Trimethylolethane	45.0	54.3	55.9

CLAIMS

1. A paper sheet support for a photographic printing paper, comprising a paper sheet on which is coated by extrusion a layer of a polyolefin in which are dispersed titanium oxide pigment particles which are coated with a dihydric, trihydric or tetrahydric alcohol.

2. A support as claimed in Claim 1, wherein said alcohol contains from 2 to 18 carbon atoms per

3. A support as claimed in Claim 2, wherein said alcohol contains from 2 to 4 methyl groups and from 2 to 6 carbon atoms per molecule.

4. A support as claimed in Claim 3, wherein said polyhydric alcohol contains 3 methanol groups and 4 or 5 carbon atoms per molecule.

5. A support as claimed in Claim 1, wherein the alcohol is trimethylolethane.

6. A support as claimed in any preceding claim, wherein said polyhydric alcohol is present in an

amount of 0.01 to 10% by weight of the weight of the titanium oxide pigment.

7. A support as claimed in Claim 6, wherein said amount is 0.1 to 1.5% by weight.

8. A support as claimed in any preceding claim, wherein said titanium oxide is present in an amount of 1 to 40% by weight of the weight of polyolefin.

9. A support as claimed in Claim 8, wherein said amount of titanium oxide is 5 to 20% by weight.

10. A support as claimed in any preceding claim, wherein the coated layer has a thickness of 5 to 200 microns.

11. A support as claimed in Claim 1, substantially as hereinbefore described with reference to any of the supports using composition (D), (E) or (F) of Example 1 or 2.

12. A photographic printing paper which has been prepared by coating, on the polyolefin layer of a support as claimed in any preceding claim, a silver halide photographic emulsion.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1982.
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.